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Conformational stability of diastereomeric 8,8-dichloro-3,5-dioxa-4-thia-4-oxobicyclo[5.1.0]octanes: X-ray crystallography, dynamic ^{1}H and ^{13}C NMR spectroscopy study

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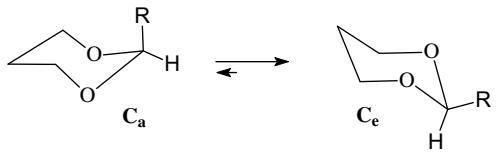
Abstract

X-ray data for both title molecules display a chair conformation with exo location of cyclopropane moiety and axial or equatorial sulfinyl group. Dynamic ^{1}H and ^{13}C NMR spectroscopy at −95 °C exhibit conformational homogeneity for the first diastereomer and two component chair – twist-boat equilibrium (2:3) for the latter.

Keywords: Heterobicyclo[5.1.0]octanes; X-ray diffraction; ^{1}H, ^{13}C NMR dynamic spectroscopy

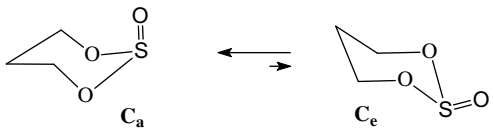
1. Introduction

Six-membered cyclic acetals and sulfites based on propane-1,3-diols belong to the known heterocycles with a well established stereochemical behaviour. The distinctive feature of the chair-like 2-*R*-1,3-dioxanes and trimethylene sulfite is the opposite tendency in conformational preference of substituents at the second position. Thus, conformational equilibria of 2-alkyl(aryl)-1,3-dioxanes are anancomerically shifted towards the forms bearing equatorial C–R bond with $-\Delta G^{0}$ values for Me and Ph amounting to 3.98 and 3.12 kcal mol^{-1}, respectively [1].



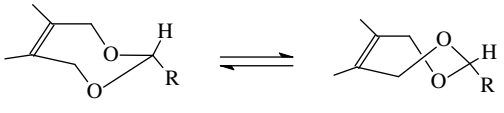
C_a C_e

Chair form of trimethylene sulfite with SO axial, by contrast, proved to be 2–3.5 kcal mol^{-1} lower in energy [2,3].



C_a C_e

Non-chair twist-boat conformations take place in these systems for sterically overcrowded molecules only [4–10]. Seven-membered acetals [11–16] and sulfites [17–22] with planar cis-butylenic and orthoxylylenic fragments exhibit examples for which chair and twist-boat forms are close enough in energy. Experimental and theoretical results demonstrate the coexistence of both conformations in solution. It is necessary to stress that among two possible chair forms only the one being more stable for six-membered molecules is established.



C_e TB

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